# Supporting Information

# Carbonate-free CoAl layered double hydroxides supercapacitors: Controlled precipitation via acid mediated decomplexation

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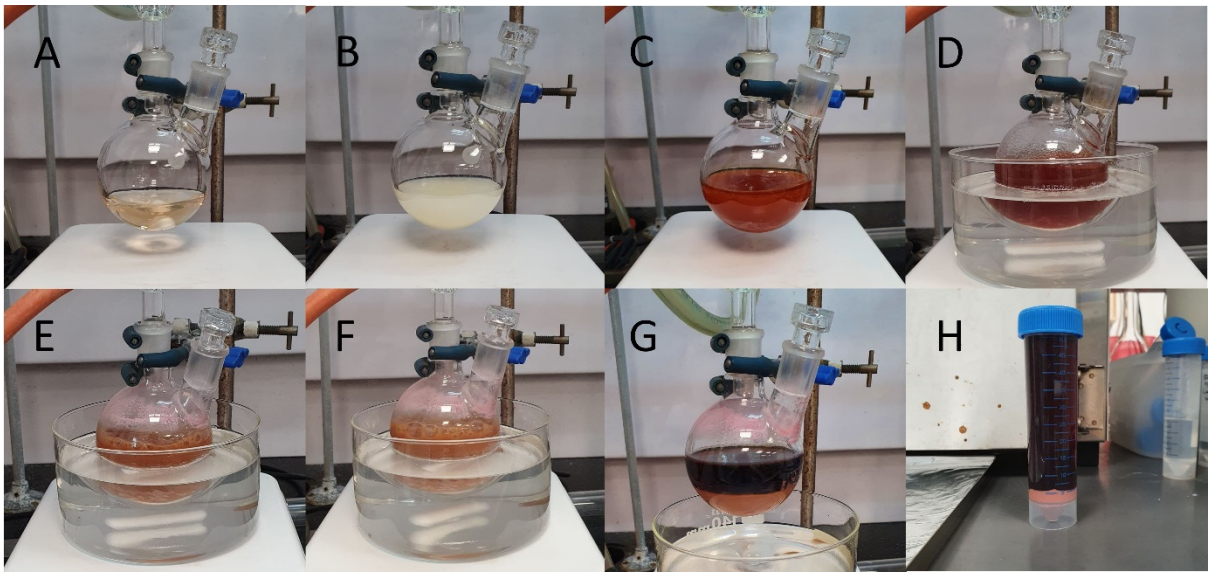


**Figure S1:** Photographs depicting the experimental observations as the synthesis progressed. Figure A: After the addition of EDA to water. Figure B: Formation of white $Al(OH)_3$ precipitate after the addition of $Al(NO_3)_3$ in $NH_4NO_3$ solution to the reaction mixture. Figure C-D: After the addition of $Co(NO_3)_2$ in $NH_4NO_3$ solution, the reaction mixture gradually turned from red to brown, signifying the formation of the $[Co(en)_3]^{2+}$ complex. Figure E-F: As the reaction progressed, the reaction changed from brown to light orange, with the precipitation of more pink CoAl LDH. Figure G: When left to settle, the reaction mixture forms a layer of pinkish orange solids at the bottom and a dark coloured solution. Figure H: After centrifuging, the suspension is separated into a dark red solution as the supernatant and pink pellet.

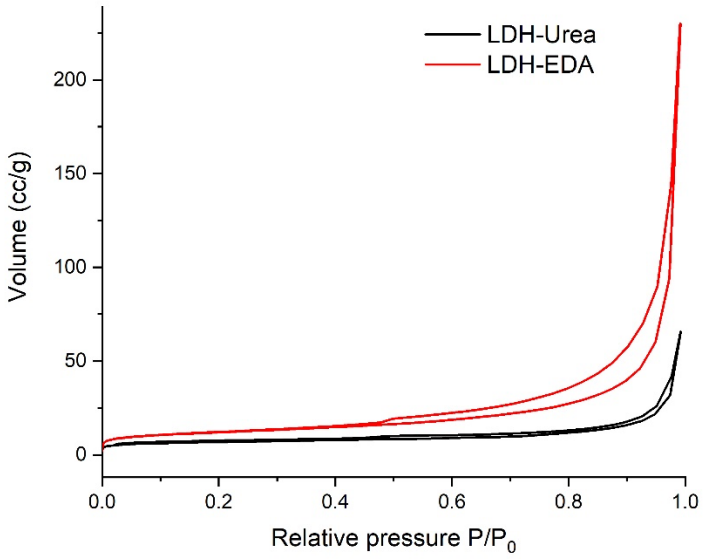


**Figure S2**: BET isotherms of LDH-EDA and LDH-Urea.

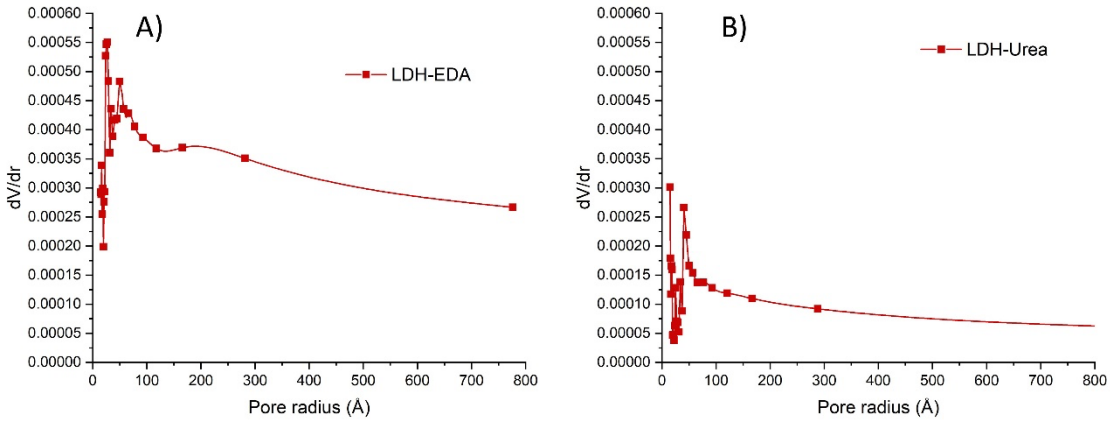


**Figure S3**: Pore size distribution plots for (A) LDH-EDA and (B) LDH-Urea

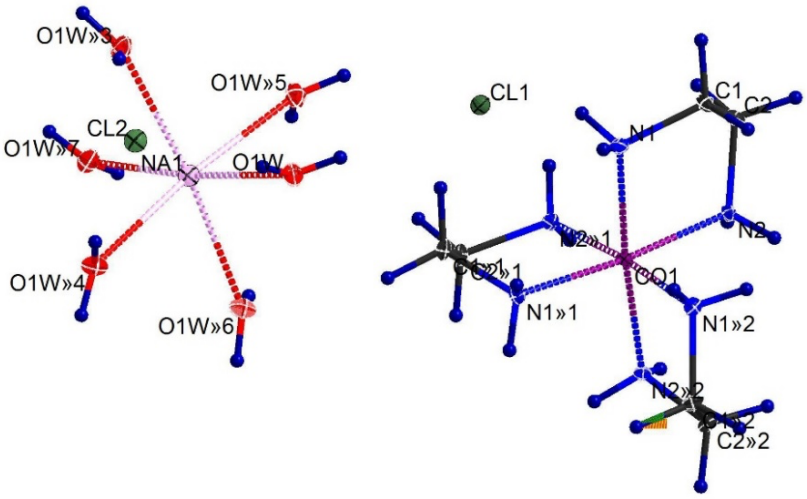


**Figure S4**: Single crystal XRD (details given in Table S1) of crystals obtained from the supernatant left behind from an in-situ anion exchange with NaCl.

**Table S1**: Crystal data and structure refinement for i263[1]

| | | |
|---|---|---|
| Identification code | i263 | |
| Empirical formula | C12 H60 Cl7 Co2 N12 Na O6 | |
| Formula weight | 857.72 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Trigonal | |
| Space group | P-3c1 | |
| Unit cell dimensions | a = 11.3212(5) Å | α= 90° |
| | b = 11.3212(5) Å | β= 90° |
| | c = 15.5994(8) Å | γ = 120° |
| Volume | 1731.50(18) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.645 $Mg/m^3$ | |
| Absorption coefficient | 1.558 $mm^{-1}$ | |
| F(000) | 896 | |
| Crystal size | 0.310 x 0.255 x 0.235 $mm^3$ | |
| Theta range for data collection | 2.077 to 30.536° | |
| Index ranges | -16<=h<=16, -16<=k<=16, -22<=l<=21 | |
| Reflections collected | 21009 | |
| Independent reflections | 1773 [R(int) = 0.0250] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7461 and 0.7019 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1773 / 0 / 86 | |
| Goodness-of-fit on $F^2$ | 1.081 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0169, wR2 = 0.0405 | |
| R indices (all data) | R1 = 0.0198, wR2 = 0.0416 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.402 and -0.580 $e.Å^{-3}$ | |

[1] CCDC 2098149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

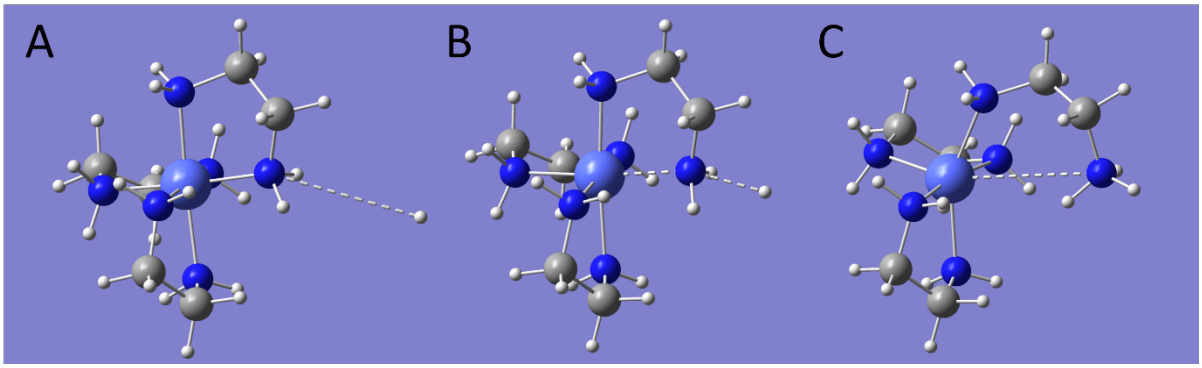


**Figure S5:** Optimised molecular structures via the protonated route where Figure A: reactant, Figure B: transition state and Figure C: product.

**Table S2:** Structural and vibrational data of the optimised molecular structures obtained via the protonated route

| | Co ─ N bond length (Å) | N ─ H bond length (Å) | Imaginary frequency ($cm^{-1}$) |
|---|---|---|---|
| Reactant | 1.98 | 3.56 | - |
| Transition state | 2.16 | 1.78 | -1329.14 |
| Product | 3.78 | 1.02 | - |

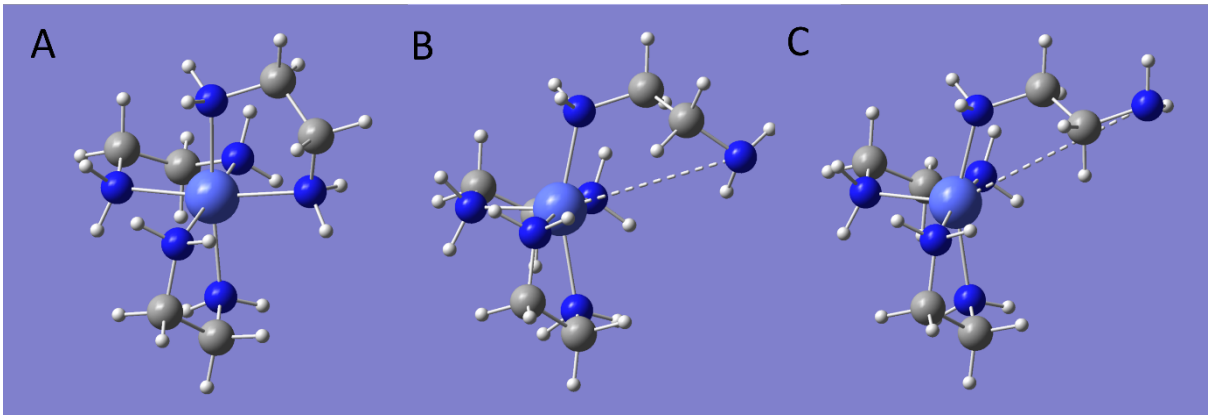


**Figure S6:** Optimised molecular structures via the non-protonated route where Figure A: reactant, Figure B: transition state and Figure C: product.

**Table S3:** Structural and vibrational data of the optimised molecular structures obtained via the non-protonated route

| | Co ─ N bond length (Å) | N─C─C─N dihedral angle (°) | Imaginary frequency ($cm^{-1}$) |
|---|---|---|---|
| Reactant | 2.21 | 54.1 | - |
| Transition state | 4.14 | 121.1 | -80.86 |
| Product | 4.97 | -176.1 | - |